

ASSESSMENT OF THE SOIL CONTAMINATION BY POTENTIALLY TOXIC ELEMENTS IN ALJUSTREL MINING AREA IN ORDER TO IMPLEMENT SOIL RECLAMATION STRATEGIES

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ABSTRACT

Land pollution due to past mining activities is a major environmental issue in many European countries. The Aljustrel mine (SW Portugal) in the western sector of the Iberian Pyrite Belt. The visual and environmental impact of the mining activity in the region is a negative consequence conditioning the population life quality, result of the pyrite and sulphides exposed to air responsible for the pollution observed in soils, superficial water and stream sediments. This paper investigates the pollution load of potential toxic elements in soil samples collected around Aljustrel mining area, in order to assess the levels of soil contamination with respect to average concentrations of toxic elements in the region and to understand the partitioning and bioavailability of pollutants in the area.

The results showed severe soil contamination (mainly As, Cd, Cu, Pb and Zn). The concentrations of As (up to 3936 mg kg⁻¹) and certain heavy metals (up to 5414 mg kg⁻¹ Cu, 61.6 mg kg⁻¹ Cd, 20000 mg kg⁻¹ Pb and 20000 mg kg⁻¹ Zn) are two orders of magnitude above the South Portuguese background values. The median concentrations of As, Cd, Cu, Pb and Zn exceed the values established for world soils, the European Union, Portugal and Andalusia. The results suggest that the distribution patterns of Co, Cr and Ni element concentrations in the Aljustrel area are primarily influenced by the lithology and geochemistry nature of bedrock. The soil background of this geological domain is characterized by relatively high heavy metal contents, essentially derived from the parent rocks.

KEY WORDS: Soil pollution; Potential Toxic Elements (PTE); Environmental geochemistry; Quality guidelines; Aljustrel mine; Iberian Pyrite Belt

INTRODUCTION

Although heavy metal mining can bring much needed economic prosperity, large areas of industrial wastelands often result once mining has ceased, with a legacy of abandoned tips and tailings, which contain the waste products of both mining and ore-processing operations (Santos Oliveira et al., 2002; Matos and Martins, 2006).

The disposal of mine wastes often produces more environmental problems than the mining operations themselves (Alvarenga et al., 2008). The piles of mine tailings (in general, fragmented and finely-ground materials) left in the vicinity, constitute one of the greatest threats, for the reason that their high concentration of heavy metals (As, Cd, Cu, Hg, Pb, Zn) and toxic chemicals, environmentally sensitive locations, unstable nature, large number and often poor to non-existent maintenance. These materials when exposed to air and water, give rise to the oxidation of remaining sulphides, through chemical, electrochemical, and biological reactions, to form ferric hydroxides and sulphuric acid combined in acidic mine

drainage (Cohen and Gorman 1991; Merson 1992; Evangelou and Zhang 1995; Larocque and Rasmussen 1998; Soucek et al. 2000).

As a direct result of the open-pit mining operations, soil is destroyed over a considerable area, and what is left of it is generally degraded and may continue causing environmental damage long after the mining period. Soil pollution with potentially toxic metals and metalloids represents one of the most prominent environmental hazards from abandoned mine lands (Thornton 1996). The soil fine fraction is usually enriched in metals, due to the relative large surface area of fine particles for adsorption and due to metal binding to iron and manganese oxides and to organic matter (Rasmussen 1998; Yukselen and Alpaslan 2001). Wind-blown dusts generated in those soils can be responsible for the atmospheric transport of trace metals (Rasmussen 1998). Therefore, soils are important sinks of heavy metals that could be inhaled, ingested, or absorbed, thereby entering the biosphere (Larocque and Rasmussen 1998). Heavy metals can persist in the soil over a long period and many of them are bioaccumulative or bio-magnified. This can result in long-term damage to flora and fauna and give rise to detrimental effects in humans, through introduction into the food chain and drinking water system.

Abandoned mines are one of the most serious environmental issues faced by many European countries and Portugal is not an exception (Pereira et al., 2004). These problems are particularly important within the mining areas where polymetallic sulphides were extracted.

In Portugal, pyrite extraction has a long tradition and represents an important industry which has given rise to several pollution problems, demanding urgent attention and remedial action (Fernandes and Henriques, 1989). Large volume of mine wastes occurs in the south of Portugal as a result of ore extracted from metalliferous mining works during the last 100 years. Approximately, 280 Mt of massive polymetallic sulfides were extracted mainly for sulfur, from about 60 mines (Strauss and Madel, 1974).

An example is the Aljustrel mine, located in SW Portugal, in the western sector of the Iberian Pyrite Belt. The large-scale and intensive mining, mineral processing and smelting activities developed in the Aljustrel region, have left a legacy of huge quantities of waste rock piles, spoil heaps and tailing ponds that cause serious environmental damage. This study rises as a consequence of two research projects, *e-Ecorisk - A regional Enterprise Network Decision Support System for Environmental Risk and Disaster Management of Large-Scale Industrial Spills* (contract n.º EV41-CT- 2002-00068) (European Project) and *EVALUSE - Environmental Vulnerability of Aljustrel Mining Area in Terms of Land Use* (a project funded by the Portuguese government). The objectives of the present study were: (1) to determine total concentrations of As and metals of major concern in soils surrounding the Aljustrel mine site; (2) to evaluate the extent of pollution in soils impacted by local mining activities and by erosion of the tailings; (3) to discuss environmental implications arising from the metal pollution load on the basis of data on metal mobility (4) and to delineate guidelines regarding future clean-up operations in the affected area and monitoring purposes..

THE STUDY AREA

Geographical location and land use

Aljustrel is located in Beja district, approximately 175 km SE of Lisbon and 125 km N of Faro (Figure 1a). Aljustrel mine is one of the great Iberian Pyrite Belt mining sites (Figure 1b), a world class volcanic hosted massive sulphides metallogenetic province (Barriga et al. 1997; Carvalho et al. 1999; Matos & Martins 2006; Oliveira et al. 2006; Relvas et al. 2006; Tornos 2006).

The Aljustrel area is located in the hydrographical Roxo River basin, being the hydrographical network well developed. From west to east the most important local streams

are: (a) Barranco do Farrôbo; (b) Água Azeda; (c) Água Forte. The Like any other part of southern Portugal, Mediterranean climate predominates in the region. The area is much warmer and receives less rainfall than the national average. The temperature reaches a maximum of 40 °C in summer (i.e., July and August) and a minimum of 5 °C in winter (i.e., December). The mean annual rainfall in the area is estimated to be 550 mm, being the period from May to September very dry and wet from October to April (in average, 85 per cent of the total annual rainfall occurs during this period). The highest amount of rainfall occurs in December, while July and August are the driest months. The catchment is dominated by rolling plains and arable lands. According to FAO soil classification (FAO, 1999), soils of the study area were classified as Leptosols (occurring over a wide variety of parent rocks, mainly metasediments and acid volcanic-sedimentary materials), Luvisols (mainly associated to slates and greywackes) and Vertisols, Luvisols, Fluvisols and Cambisols associated to conglomerates and sandstones. Natural vegetation is mainly composed by *Quercus rotundifolia*, *Cistus ladanifer*, *Genista hirsute*, *Cistus salviifolius*, *Cistus crispus*, *Cistus monspeliensis* e *Lavandula luisieri*. In Aljustrel area the *Quercus* forests have been replaced by eucalyptus plantations (*Eucalyptus camaldulensis*).

Geology and mineralization

According to Schermerhorn & Andrade (1971), Barriga (1990), Barriga & Fyfe (1988), Barriga *et al.*, (1997); Relvas *et al.* (1990), Dawson *et al.* (2001), Carvalho *et al.* (1999) among others, the geology of Aljustrel region is characterized by a Palaeozoic basement of the South Portuguese Zone and by a modern sedimentary sequence of the Alto Sado Tertiary Basin (USTB). The active NE-SW Messejana fault defines the SE border of this basin, which is confined to the NW block of the fault (Fig. 1c).

Fig. 1

The Messejana fault presents an Iberian dimension and a senestral strike-slip movement of 2.5 km. This fault separates the Sado Tertiary Basin (NW side of the fault) of the Paleozoic (SE margin). Along this major structure a Jurassic dolerite (MD) is also observed (Schermerhorn *et al.* 1987).

According to several authors (Andrade & Schermerhorn 1971; Schermerhorn and Stanton 1987; Silva *et al.* 1997; Leitão 1998; Matos 2005; Oliveira *et al.* 2006), the Aljustrel's Palaeozoic stratigraphic sequence is formed by the following main units: Baixo Alentejo *Flysch* Group (MFF): Mértola Formation (Upper Visean) – shales and greywackes (*flysch* turbidites). The Iberian Pyrite Belt: Volcano-Sedimentary Complex (VSC) (Upper Famennian – Upper Visean) represented by the following units: Paraíso Fm. – siliceous shales, phyllites, tuffites, purple shales, jaspers and cherts; felsitic/mine metavolcanics and green metavolcanics sequences – sericitic felsic volcanics, felsites, felsophyres, volcanic breccias, massive sulphides, feldspar megacryst volcanics and lavas. The IPB lower unit, the sedimentary Phyllite-Quartzite Group (Frasnian-Upper Famennian), is not recognized in the Aljustrel area. The VSC Aljustrel Anticlinorium is represented by a NW-SE lineament (4.5 km length and 1.5 km across).

In the Aljustrel mining site, six massive sulphide orebodies are recognized along a 6Km structure of Vulcano-Sedimentary Complex: Moinho, Feitais, Estação, Gavião, Algaes and São João, the last two were mined since Roman times (Silva *et al.* 1997; Leitão 1998; Matos & Martins 2003, 2006). Moinho deposit was exploited by the Pirites Alentejanas Company (PA) for copper until 1993. The gossans and the supergene zones of the Algaes and São João orebodies were exploited during roman era to 100 m deep (Domergue 1983). These massive sulphide orebodies have a simple mineralogy composed mainly by pyrite (FeS_2) (> 70%), with minor quantities of sphalerite (ZnS), chalcopyrite (CuFeS_2), galena (PbS), arsenopyrite (FeAsS), tetrahedrite ($(\text{Cu,Fe})_{12}\text{Sb}_4\text{S}_{13}$), arsenopyrite (FeAsS), bornite (Cu_5FeS_4), pirrotite (Fe_{1-x}S ($x=0-0.17$)) e cassiterite (SnO_2) and sulfosalts (Matos & Martins, 2006). The Mn mineralization is composed, essentially, by Mn oxides, namely pyrolusite

[MnO₂] and psilomelane [MnO₂], where is also possible to find limonite [2Fe₂O₃.3H₂O], hematite [Fe₂O₃] and baritine [BaSO₄].

Mining activity and environmental impact in the Aljustrel area

In result of thousands of years of intense pyrite ores exploitation in Aljustrel, large areas are now occupied by several waste tailings such as Roman slag, pyrite ore (blocks and brittle massive pyrite ore – the most reactive ones) and Volcano Sedimentary Complex host rocks. Algaes industrial area and São João do Deserto sector present the highest volumes of mine waste. The total amount of waste stored on the site exceeds 3Mt (Matos & Martins 2006). Those areas are affected by strong pluvial erosion, no vegetation and visible intense AMD. The small Mn-Fe exploitations are represented by small open pits and associated ore tailings, usually with less than 1 m thickness. Part of these small mines is used for illegal waste disposals. The environmental impact of these Mn-Fe exploitations is not quantified but is certainly locally significant. Other wastes are present in Aljustrel, with less contaminant potential like host rocks, represented by felsic well cleaved and coherent volcanics, siliceous, purple and black shales, jaspers and cherts (Volcano Sedimentary Complex host rocks). Roasted pyrite ore has a very low expression confined to spotty occurrences at Algaes. Some of the mining infrastructures are unsafe and potentially dangerous, like open pits, quarries, galleries and mining shafts very exposed to local urban areas (Matos & Martins 2006). The walls of São João do Deserto open pit and Malpique and Moinho quarries present significant geotechnical instability.

MATERIALS AND METHODS

Field sampling and chemical analysis

To investigate the impact caused by the dismantling and erosion of the tailings around the Aljustrel mine site, soil samples were collected in the area and analyzed. Soils were sampled on two occasions: the first sampling occurred during the summer of 2005 and encompassed soils from the VSC and MFF host rocks, and the second sampling occurred in the summer of 2006 and encompassed soils from the USTB. The studied area was monitored with a sampling network established on a 250-250 m grid in the centre of the contaminated area and 500-500 m in the remaining area (Figure 1c). Each sampling point was georeferenced by Global Positioning System (GPS). A total of 356 soil samples were collected over an area of 44 km², corresponding to a sampling density of 8 samples km². At each sampling point, the surface of the soil was cleared of superficial debris, vegetation and the O-soil horizon. A composite sample consisting of three subsamples was collected (with a minimum distance between subsamples of 3 m) from the topsoil. According to the established grid the representativeness of the collected samples with the rock parent material is: 42.4% of samples is related with Tertiary Sado Basin Sediments (USTB); 1.7 % with Messejana Dolerites (MD); 36.8% with Baixo Alentejo Flysch group (MFF) and 19,1% with Volcano-Sedimentary Complex (VSC). After collection, the soil samples were dried in an oven at a temperature of 40 °C, until a constant weight was attained, disaggregated and passed through a 177 µm aperture plastic sieve.

Surficial mine waste samples (upper 5 cm) were sampled by collecting 10-increment composites. About 1kg of each sample was crushed with a jaw crusher and pulverized in a mechanical agate mill. The samples were reduced to 250g by coning and quartering, followed by drying at 40°C. After homogenization aliquots of 30-50g of each dried sample were powdered in a mechanical agate mill.

The fine grained fraction of soil and mine waste samples were submitted to multi-elemental analysis in an accredited Canadian laboratory (ACME Anal. ISO 9002 Accredited Lab-Canada). A 0.25 g split was leached in hot (95°C) aqua regia (HCl-HNO₃-H₂O) for 1 hour and diluted with 10 ml of desmineralized water. Total concentrations (detection limits between brackets) of As (0.5 mg kg⁻¹), Cd (0.1 mg kg⁻¹), Co (0.1 mg kg⁻¹), Cr (1 mg kg⁻¹), Cu (0.1 mg

kg⁻¹), Ni (0.1 mg kg⁻¹), Pb (0.1 mg kg⁻¹) and Zn (1 mg kg⁻¹) were determined by Inductively Coupled Plasma-Emission Spectrometry (ICP-ES OPTIMA). The accuracy and analytical precision were determined using analyses of reference materials (standards C3 and G-2) and duplicate samples in each analytical set.

Mineralogical studies

Minerals of the tailings samples were determined by powder XRD using a Phillips powder diffractometer, model PW3040/601, equipped with an automatic slit. A Cu-X-ray tube was operated at 40 kV and 30 mA. Data were collected from 2 to 70° 2 θ with a step size of 1° and a counting interval of 0.6 seconds.

Selective Chemical Extraction Procedure

Chemical forms of heavy metals in soils directly influence their bioavailability and toxicity (Tessier et al. 1979; Ma & Rao 1997; Zhou & Sun 2002; Zhou et al. 2004). Trace metals can be transported in the secondary geological environment by different chemical mechanisms (Gibbs, 1973): a) in solution or adsorbed on solids, being readily available in these conditions; b) in organic compounds or metallic hydroxides, for which chemical changes are required before they are released; c) in the crystal structure of some minerals, where they are generally unavailable for the ecosystems.

Many schemes of sequential extraction to assess chemical speciation have been developed. In these schemes, samples are sequentially treated with different reagents in order that metals with different affinities for the mineral matrix can be liberated (Tessier *et al.*, 1979; Meguellati *et al.*, 1983; Rapin & Forstner, 1983; Quevauviller *et al.*, 1994; Gomez-Ariza *et al.*, 2000).

A sequential chemical extraction procedure proposed by Cardoso Fonseca (1984) was adopted in this study. Reagents were applied sequentially to the solid phase of selected samples, according to their chemical aggressiveness. The extractable fractions of As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were obtained by extraction with different solutions: (a) 1st Step - sodium acetate (NaOAc, pH 5) for extraction of exchangeable cations adsorbed by clay and co-precipitate by carbonates, to which are associated elements depending on pH for solving; (b) 2nd Step - cold hydroxylamine for extracting amorphous Fe oxides and crystalline Mn oxides; (c) 3rd Step - hot hydroxylamine for extraction of amorphous and crystalline Fe oxides and crystalline Mn oxides; (d) 4th Step - aqua regia, for extracting sulphides on clay minerals; (e) 5th Step - four acids digestion (or total attack) where the remaining silicate will be decomposed.

Selected samples for this SCE study were J6, K3, L5 and N5 (Figure 1c). This selection was based on the As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn chemical analysis. The soil samples used in the SCE experiments were air-dried, disaggregated and sieved through a 177 μ m aperture plastic sieve. The fine grained (<177 μ m) fraction of soil samples was submitted to sequential chemical extraction procedure in ACTLABS accredited laboratory.

The accuracy of the sequential treatment, considered as a whole, was estimated by the comparison of the total sum of the amounts obtained after each sequential extraction step with the total amount obtained after hot mixed-acid attack of the same sample. For all the extractions, the total of the trace elements in the different fractions did not exceed $\pm 10\%$ of the bulk sample which is accepted as satisfactory (Tessier et al, 1979; Pickering 1986; Yan et al, 1999).

Data Analysis

Statistical data analysis is a powerful tool in monitoring soil properties and assists in the interpretation of environmental data (Tuncer, 1993; Einax and Soldt, 1999). In recent times, statistical methods have been applied widely to investigate heavy metals concentration, accumulation and distribution in soils. This is documented by a large number of reported studies which apply statistical methods to heavy metals in soils. Salman et al. (1999), Yu-Pin

Lin (2002) and Qishlaqi and Moore (2007) have used multivariate statistical methods to study the behaviour, distribution and interrelationship of heavy metals in soils. Therefore, statistical analysis of heavy metals in soil can offer an ideal means through which to monitor not only the heavy metals accumulation in soil but also the quality of the overall environment as reflected in soil.

Spatial Estimation: variography provides a description of the spatial pattern of a continuous attribute Z (or an indicator variable I_c), say a pollutant concentration of a chemical element (Reis et al., 2005) or the anomalous concentration of a metal orebody with economic interest (Reis et al., 2003; Patinha et al., 2008). Given a data set for the variable Z at n locations x_i , ($Z(x_i)$, $i = 1, 2, \dots, n$), the sample variogram $\gamma_Z^*(h)$ – the symbol $*$ in this text will indicate estimates – measures the average dissimilarity between data separated by a vector h (Goovaerts, 1999),

$$\gamma_Z^*(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(x_i) - Z(x_i + h)]^2 \quad (1)$$

where $N(h)$ is the number of data pairs at a lag of h . For I_c , the variogram is,

$$\gamma_{I_c}^*(h) = \frac{1}{2N(h)} \sum_{j=1}^{N(h)} [I_c(x_j) - I_c(x_j + h)]^2 \quad (2)$$

The variogram can be calculated for different directions of h , which allows us to know how the variable $Z(x)$, or $I_c(x)$, varies in several directions of the space.

Ordinary kriging: the main application of geostatistics to soil science has been the estimation and mapping of soil attributes in unsampled areas. Kriging is a generic name for a family of spatial least-squares predictors. For the prediction of the variable Z at a location x_0 , $\{Z(x_0)\}$, the estimator $Z^*(x_0)$ is defined as (Goovaerts, 1999):

$$Z^*(x_0) = \sum_{i=1}^n \lambda_i Z(x_i) \quad (3)$$

where the λ_i are weights found by solving the system of equations,

$$\sum_{j=1}^n \lambda_j \gamma(x_i, x_j) + \mu = \gamma(x_i, x_0), \quad i = 1, \dots, n$$

$$\sum_{j=1}^n \lambda_j = 1$$

with $\gamma(h)$ being the theoretical model for the variogram of the variable Z (fitted to the sample variograms) and μ being a Lagrange multiplier.

Contamination Factor and Modified Degree of Contamination: Hakanson (1980) proposed an overall indicator of contamination based on integrating data for a series of specific heavy metals. This method is based on the calculation for each pollutant of a contamination factor (C_f). The C_f is the ratio obtained by dividing the mean concentration of each metal in the soil (C_i) by the baseline or background value of the specific metal (C_b) Liu et al. (2005):

$$C_f = C_i / C_b$$

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C_f is defined according to four categories as follows (Liu et al. 2005):

$C_f < 1$ - low concentration factor

$1 < C_f < 3$ - moderate contamination factor

$3 < C_f < 6$ - considerable contamination factor

$C_i > 6$ - very high contamination factor

Abraham (2005) presented a modified and generalized form of the Hakanson (1980) equation for the calculation of the overall degree of contamination as below.

$$mC_f = \left(\sum_{i=1}^n C_f \right) / n$$

where:

n = number of analyzed elements and i = i th element (or pollutant) and C = Contamination factor.

For the classification and description of the modified degree of contamination (mC_f) in soil the following gradations are proposed by Abraham and Parker (2008):

- $mC_f < 1.5$ - Nil to very low degree of contamination
- $1.5 < mC_f < 2$ - Low degree of contamination
- $2 < mC_f < 4$ - Moderate degree of contamination
- $4 < mC_f < 8$ - High degree of contamination
- $8 < mC_f < 16$ - Very high degree of contamination
- $16 < mC_f < 32$ - Extremely high degree of contamination
- $mC_f > 32$ - Ultra high degree of contamination

RESULTS

Distribution of PTE in topsoil

A global dataset composed by 356 soil samples and 10 variables (As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn concentrations) was assembled. A descriptive statistical analysis permit to describe and resume a set of data that allows finding the anomalous structures presents. Descriptive statistical parameters for trace elements for global data and categorized according to the parent rock lithology are summarized in Table 1. These values were compared with As, Cd, Co, Cr, Cu, Ni, Pb and Zn reference median values reported in worldwide soils (Global soil mean - Reimann and De Caritat, 1998), European Union (Levinson, 1980), South Portuguese zone and Andalusia (Galán et al., 2002, 2008) listed in Table 2. In this study, the concentration of potentially hazardous trace elements and extent of pollution load have been quantified and related to soil quality guide values such as the Portuguese (Ferreira, 2004), Andalusia (Galán et al., 2002, 2008) and Netherlands (Alloway, 1995).

The total As content in soil samples from Aljustrel area varies between 6 mg kg^{-1} and 3936 mg kg^{-1} , with a median value (18 mg kg^{-1}) similar to the topsoil baseline for As in the SPZ (21 mg kg^{-1}). However the median values are quite different depending on the location of the samples with respect to parent rock material (Table 1). The samples collected in the VSC units are clearly the most enriched soils exceeding in some cases 14.5 times the SPZ baseline. These values clearly exceed the median As concentrations for soils of the world (5 mg kg^{-1}), the European Union (7 mg kg^{-1}), and the baseline values for Portugal and also the Andalusia region (10 mg kg^{-1}). The As threshold value of the SPZ (179 mg kg^{-1}) is also exceeded in soils collected in the VSC and MFF geological units (circa 8% of soil samples exceeded the threshold value). The distribution of high values is related to sulphide ore occurrence and mining activities. Some samples collected in the vicinity of Algarés and S. João do Deserto are in the range of values above which toxicity is considered to be possible (Kabata-Pendias and Pendias, 1992).

The total Cd content in the Aljustrel soil samples ranges from 0.1 to 61.6 mg kg^{-1} , with 0.2 mg kg^{-1} as a median value. This median value is lower than the one for world soils (1 mg kg^{-1})

the European Union soils (0.3 mg kg^{-1}) and Portuguese soils ($< 0.2 \text{ mg kg}^{-1}$). Locally, some soils remain enriched in Cd (concentrations ranging from 1.0 to 61.6 mg kg^{-1}) representing 4.5% of the total samples. These extreme values are registered in soils related to the VSC, MD and MFF geological units.

In the Aljustrel area, the median for Co (16 mg kg^{-1}) are similar to the corresponding values in the SPZ (19.0 mg kg^{-1}) while the threshold value in the SPZ is 36 mg kg^{-1} . The extreme values observed in the VSC and MFF units may have a geologic origin because they apply to soils developed on shales and greywackes (flysch turbidites), phyllites, tuffites, purple shales, jaspers and cherts, sericitic felsic volcanics, felsites, felsophyres, volcanic breccias, massive sulphides, feldspar megacryst volcanics and lavas with high Co contents. The high Co concentrations in soil may also be due to adsorption and coprecipitation involving Fe and/or Mn from parent rocks rich in these metals or from mineralisation (Salminen and Tarvainen, 1997). The median values for Co observed in the Aljustrel area are similar for all the soil derived from the different parent-rocks categories (16 mg kg^{-1}), however this value is also higher than that for the world soils (10 mg kg^{-1}) the European Union soils (8 mg kg^{-1}) and the baselines of Portuguese (8 mg kg^{-1}) and Andalusia soils (12 mg kg^{-1}).

The total Cr content in soil samples from Aljustrel area varies between 6 mg kg^{-1} and 115 mg kg^{-1} , with a median value (56 mg kg^{-1}). The median values observed in soil samples derived from the different parent-rocks categories are below the SPZ threshold value (248 mg kg^{-1}). The outlier values are related to basic intrusive and volcanic rocks, and other Cr-rich parent rocks, such as metabasites. Based on this geochemical relationship between Cr content in topsoil and specific lithology of the bedrock, it is likely that the Cr outliers have a geologic origin.

The total Cu concentration ranges between 10 to 5414 mg kg^{-1} , with a median of 39 mg kg^{-1} (the median value of Cu in topsoil is 32 mg kg^{-1} in the SPZ, Galán et al., 2008). The baseline levels in the Aljustrel are also above the median of the Cu concentrations in soils of the world (25 mg kg^{-1}), the European Union (13 mg kg^{-1}) and Andalusia region (24 mg kg^{-1}). In the Aljustrel area the high Cu contents of topsoil appear to be associated with acid volcano-sedimentary rocks (VSC). The Cu content of anomalous samples of VSC surpasses the threshold values of the SPZ for topsoil (147 mg kg^{-1} - Galán et al., 2008) indicating a probable relation with regional and local mineralization and with the mining wastes (some samples show a topsoil/parent rock ratio ranging from 10 to 140).

The total Ni content in soil samples from Aljustrel area varies between 2 mg kg^{-1} and 106 mg kg^{-1} , with a median value (30 mg kg^{-1}). The median value obtained for the Aljustrel database is very similar to the baseline levels for Ni in the SPZ (37 mg kg^{-1}) and are well above those for soils of the world (20 mg kg^{-1}) and the European Union (18 mg kg^{-1}), and slightly exceed the regional "background" value for the Portuguese and Andalusia soils (16 and 29 mg kg^{-1} , respectively). All the values, except for soil samples derived from the MFF geological unit do not exceed the threshold values for Ni in the SPZ (63 mg kg^{-1}). The anomalous MFF samples derived from shales and greywackes (flysch turbidites). In most of these sampling sites, the topsoil/parent rock ratio is low, indicative of a lithological origin.

The median Pb content in the Aljustrel area is about 38 mg kg^{-1} , although some extreme values (up to 20000 mg kg^{-1}) were recorded. The study area records exceed the threshold value for Pb in the SPZ (205 mg kg^{-1}) in the VSC, MD and MFF related soil samples (11% of soil samples surpass the threshold value). The median values obtained in these areas exceed the "backgrounds" estimated for soils of the world (70 mg kg^{-1}), the European Union (52 mg kg^{-1}) and the Portuguese and Andalusia soils (21 and 56 mg kg^{-1} , respectively). The extreme values are given in topsoil samples from the VSC and MFF geological units. These soils samples derived from acid volcano-sedimentary materials of the Iberian Pyrite Belt. The maximum Pb concentration (20000 mg kg^{-1}) observed in these samples show a topsoil/parent rock ratio ranging from 10 to 526 indicating contamination from mining operations.

The total Zn content in the Aljustrel soil samples ranges between 22 and 20000 mg kg⁻¹ with an median value of 88 mg kg⁻¹, which is slightly above the baseline concentration in the SPZ (76 mg kg⁻¹). The median value obtained for the Aljustrel soils exceed the median Zn concentrations in world soils (70 mg kg⁻¹), the European Union (52 mg kg⁻¹) and the Portuguese and Andalusia soils (55 and 56 mg kg⁻¹, respectively). The threshold value for Zn in the in the SPZ (173 mg kg⁻¹) is exceed in 17% of samples. The extreme Zn concentrations (up to 20000 mg kg⁻¹) occur at the top of the soils from parent materials belonging to the volcano-sedimentary complex of the Iberian Pyrite Belt. The topsoil/parent material ratio varies widely between 3.6 and 9.4 in the OMZ, and from 0.2 to 263. The origin of this Zn enrichment seems to result from sulphide mineralization and anthropogenic pollution due to mining activities.

Partitioning of metals in selected samples

Determining the total concentrations provides insight about the extent of metal accumulation and the pollution load, but does not properly describe the environmental risk of the potentially contaminated soils since not all the metals present in the soil are biologically available (Li and Thornton 2001). Four samples (K3, N5, L5 and J6 – see figure 1c) were selected for the sequential leaching of heavy metals according to the results obtained.

The XRD results show that the mineralogy of the different selected soil samples is very similar. Soil samples are commonly composed of quartz (SiO₂), plagioclase (Na,Ca)(Si,Al)₄O₈, phyllosilicates (Al₂Si₂O₅(OH)₄). The soil samples are characterized, in most cases, by the presence of remarkable amounts of iron oxy-hydroxides [goethite (FeOOH), hematite (Fe₂O₃), magnetite-maghemite (Fe₃O₄-(Fe₂O₃)] and sulfates, mainly jarosite (KFe^(III)₃(OH)₆(SO₄)₂), alunite (KAl₃(SO₄)₂(OH)₆), anidrite (CaSO₄), gypsum (CaSO₄·2H₂O) and thernardite Na₂SO₄], derived from an active sulfuricization process. Iron oxy-hydroxides usually occur as extremely fine grained, poorly crystalline aggregates and coatings. The soils still can contain some crystals of reactive sulfide such as pyrite, arsenopyrite and galena. Punctually some siderite (FeCO₃) and plumbogummite (PbAl₃(PO₄)₂(OH)₅·(H₂O)) occur in the studied samples. The clay mineral assemblage identified by XRD is dominated by kaolinite, with minor poorly defined mixed-layer minerals.

The affinity of metal concentrations in five geochemical fractions (metal bearing-phases) is presented in Figure 2. The results show that the most important As bearing-phases, for the four selected samples are the sulphides and clay minerals (arsenic was extracted mainly by aqua regia, with the percentage of extraction ranging between 82% to 93% - samples N5, K3, L5, in ascending order of percentage of extraction). Some As is also linked to the Fe crystalline oxides (N5 -13% and J6 – 5%). It should be noted, taking into account the results of the mineralogical study of samples, that As may be associated with the presence of arsenopyrite and may also be associated with magnetite and iron pyrite. Moreover the percentage of extraction with sodium acetate, pH 5.0 (extraction of exchangeable cations and clay items added by the co-precipitated as carbonates) in the studied samples are very low in most samples, but sample N5 show a value of 0.32% of extraction. These results can become very important, because the As concentrations associated with this percentages of extraction (4.5 mg kg⁻¹) are high, accounting for a significant amount of As in bioavailable form. According to Reiman & Caritat (1998), values greater than 0.06 mg L⁻¹ in water requires remediation of contaminated site.

Cadmium (Figure 2) also shows, as major bearing-phases, sulphides and clay minerals (with percentage of extraction of aqua regia to vary between 20.6 and 55.9% - most representative in samples K3, L5, J6,) and remaining silicates (the percentage of extraction vary between 17.3 and 28.0% - most representative in samples K3 and J6 to total attack). It is worth nothing that in some sample a significant percentage is linked to exchangeable cations/adsorbed and Fe/Mn amorphous and crystalline oxides. Taking into account the results one can say that the presence of Cd is justified by the occurrence of sphalerite in the soil samples. Sphalerite was not been identified by XRD because mineralogical

characterization by XRD does not allow the detection of mineral phases present in small proportions, which could be a point of interest since Cd usually replaces Zn in the crystalline network of the sphalerite. Among these results should be highlighted the percentage of extraction with sodium acetate (pH 5.0) obtained in all samples, meaning that a significant amount of Cd is associated to exchangeable cations or adsorbed, representing its readily available forms of Cd. According to the results its concentrations of Cd readily available may vary from 0.48 to 0.69 mg kg⁻¹. According Reiman & Caritat (1998) values of Cd concentration over 0.004 mg L⁻¹ in water samples require remediation.

For Co (Figure 2), the results show clearly the dominance of silicate minerals as metal bearing-phases (the % of extraction ranges between 50.4 and 80.7%). The results are in agreement with the VMS geological context.

Chromium results show that a large proportion of this element is associated with silicate minerals (the % of extraction ranges between 50.4 and 80.7%). The results are in agreement with the geological context. It is recalled that the parent rock lithology of samples K3, N5, L5 and J6 is the Paraiso Formation, represented by siliceous shales, phyllites, tuffites, purple shales, jaspers and cherts; felsitic/mine metavolcanics and green metavolcanics sequences – sericitic felsic volcanics, felsites, felsophyres, volcanic breccias, massive sulphides, feldspar megacryst volcanics and lavas. Most of the Cr concentrations in the selected samples are very low.

The SCE results shows that Cu sulphides and clay minerals (with percentage of extraction of aqua regia (Step 4) varying between 43.2 and 65% - samples K3 and L5, respectively) and silicates (percentage of extraction, the total attack (Step 5), vary between 5.7% and 22.2% - J6 and N5, respectively), as the most important bearing-phases of Cu. However it appears that the percentages of extraction cold hydroxylamine are also significant (percentage of extraction ranging between 18.9 and 27.9%) demonstrating an important contribution of amorphous iron oxides and manganese oxides. Punctually Fe/Mn crystalline oxides represent also an important Cu metal bearing-phase (17% of extraction in sample J6 by hot hydroxylamine). Similarly to sphalerite, chalcopyrite was not identified by XRD analysis. The percentage of extraction with sodium acetate (pH 5.0) obtained in all samples (values ranging between 0.6 to 13.8%) indicates that an important amount of Cu (0.9 to 170 mg kg⁻¹) could be easily available.

Figure 2 show that Ni is preferably linked with sulphides and clay minerals (percentage of extraction, the aqua regia, varying between 43 and 76.3% - J6 and L5, respectively) and also with remaining silicate minerals (with a percentage of extraction, ranging between 7.9 and 51.4% - L5 and J6, respectively). The total Ni concentrations in the selected samples is very low (4 – 11 mg kg⁻¹) but it should be noted that the percentage values obtained for sodium acetate extraction are relatively high in some samples (11.3% - L5; 12.9% - N5; 27.7% - K3), meaning that Ni could be associated to the interchangeable fraction and be easily mobilized.

Lead concentrations are extremely high (values ranging between 2020 and 20000 mg kg⁻¹) in the selected samples. According to the results Pb appears associated to sulphides (34 to 84 % of extraction associated with Step 4), but also it is associated with the remaining silicates (14 to 45% of extraction associated with Step 5). The results indicate that, for most samples, the presence of galena (PbS) is responsible for high Pb concentration in soil samples, since the percentage of lead extracted by aqua regia is important. It appears that the residual values of silicate shows high percentage of extraction. Should not be put aside the importance of hydroxides of Pb, represented in the sample K3 by plumbogummite (PbAl₃(PO₄)₂(OH)₅. (H₂O)). In addition, the results evidence that in some samples Pb may be also interchangeable (2.8 to 6.1%).

Like Pb, Zn concentration is also very high (levels ranging between 422 and 2378 mg kg⁻¹). Zinc was found essentially associated to Zn sulphides and clay minerals (percentage of extraction, the aqua regia, ranging between 65 and 72% - samples J6 and N5, respectively).

It can be noted that a significant proportion of zinc is associated with amorphous Fe oxides (7.2 to 23.6% of extraction – N5 and K3 respectively).

The values of percentage of extraction obtained for the sodium acetate, (ranging between 3.4 and 42% - L5, K3) justify emphasis. Considering the high total Zn concentrations, the values of available Zn (such as 174 and 265 mg kg⁻¹ in samples K3 and N5), can be easily mobilized to the water surface and interfere with the local runoff. As one would expect the images obtained for the Zn and Cd are similar, which indicates a strong correlation between these two elements since they are associated with the same metal bearing-phase (sphalerite).

Iron, as expected due to the sample mineralogical composition, is basically found distributed in two fraction: sulphides (main fraction – in average 88 % of extraction) and also with iron and manganese oxides (3.8 to 9.8 % of extraction – see Figure 2). This distribution is very similar to that obtained for As. Manganese is associated with the sulphides/clay minerals and with the remaining silicates fraction. It is also found an important proportion in the fraction associated with the interchangeable/adsorbed/co-precipitated of carbonates fraction (24.6 to 40.9% of extraction). The presence of jarosite in topsoils creates an additional contamination problem since jarosite-type phases act as temporary storage for acidity and may release this stored acidity upon hydrolysis and redissolution (Miller, 1995).

The partitioning data obtained shows that most of the elements were mainly associated with the sulphides/clay minerals and the residual fraction of the soil (for As, Cu and Pb, more than 70% of the total metal content was in the residual fraction). The metal extracted by the first step was less than 5% of the total content for As, Cu and Pb. The exception was Cd and Zn were the metal extracted by the first step ranged between 10 and 40%. The fraction extracted by the first step is according Kennedy et al. (1997) considered a relative empirical estimate of metal bioavailability.

Environmental quality and remediation actions

In this study, a simplified approach to risk assessment based on comparing the measured level of contamination in the Aljustrel soils with local median values (Table 1) were adopted. Table 3 shows the results of contamination factors considering the global data and the data categorized according to the parent rock lithology.

The results reveal that globally the Aljustrel area presents a moderate degree of heavy metal contamination. According to the results the contamination factor for As and Pb are considerable and moderate for Cd, Cu and Zn. The highest C_f is observed for Pb which is significant in soils from the VSF and MFF geological units. The soil samples from the MD geological unit reveal noticeably contamination in Zn and Cd. Revised Hakanson equation was used to calculate the modified degree of contamination (mC_f) for the eight analyzed elements (Table 3). The range of mC_f values (1.10-12.3) indicates a low to moderate degree of contamination in the Aljustrel area being particularly higher in soils from the VSC and MFF geological units. According to the results the USTB soils are considered as not contaminated or with low contamination. According to the contamination factors values among the eight metals tested, As, Cd, Cu, Pb and Zn were the elements of most concern whereas Co Cr and Ni show values near 1 meaning that were not significantly pollution occur in the area.

Soil quality for environmental purposes can be measured in many different ways (e.g. Pierzynski et al., 1994; Sims et al., 1997; Galán et al., 2002). In this work the Andalusia (Galán et al, 2002) and the Portuguese (Ferreira, 2004) quality standards were adopted for comparison and to establish recommendations for soil management. Figure 3 to 7 presents maps of As, Cd, Cu, Pb and Zn spatial distribution, according to the soil management guidelines. Table 4 presents the sample distribution between the different classes taking in consideration the Andalusia Guide Values.

The pattern presented by As, Cu, Pb, Zn suggest that the area surrounding the Algaes (A) and S. João do Deserto (b) mines needs intervention. According to the Andalusia guide

values there were 17.1%, 5.3%, 6.7% and 1.7% of soil samples that fall in the Class 4 (intervention is needed) because they are polluted by As, Cu, Pb and Zn, respectively (Table 4). Among the five metals, As and Pb ranked the first two polluted elements in term of the extent of contamination. According to the Portuguese guide values there were 18.0%, 46.6%, 19.4% and 46.6% of soil samples that fall in the Class 4 (intervention is needed). The differences obtained for the Cu, Pb and Zn variables are explained by the enrichment of the local geological formations in these elements.

These results are of most importance since an exchangeable fraction of As and Pb were detectable in some soil samples, as noted in the selective chemical extractio. Also, from Cd pattern is possible to conclude that punctual Cd contamination occurs in the S. João do Deserto area based on the assessment method. According to Glanzman & Closs (1993), Cd is considered a priority pollutant metal, meaning that is of great interests for environmental impact studies.

As noted above, the soils close to the mining areas retain anomalously high concentrations of a cocktail of potentially toxic elements rather than only one pollutant. Considering the A and B areas individually, the metal content is much greater than that of the local soils, and even they are above the maximum concentrations recommended for agricultural soils (see values of CSTC in Table 2). It is possible to perceive that the mean variation ranges of As (232-992 mg kg⁻¹), Cd (1.8-9.1 mg kg⁻¹) Cu 688-943 mg kg⁻¹), Pb (757-5156 mg kg⁻¹) and Zn (851-3421 mg kg⁻¹) are significant higher showing clearly an increase in C_f values. In the Algaes area As e Pb are the elements which present the highest C_f values (Table 3) while in the S. João do Deserto Cd and Zn represent the elements of concern (highest C_f for both elements). Comparing the two areas, the Algaes and S. João do Deserto, present a similar degree of contamination (see Table 3). These elements are delivered from tailings and mine-waste tips to soils by wind, as dust particles, or by acid mine drainage in dissolved and particulate forms.

The mine waste materials in the Algaes e São João do Deserto areas are undergoing reactions with air and rainwater. The exposure of pyrite-rich ore stockpiles and waste dumps to weathering processes led to the precipitation of white, green and yellow sulphate efflorescences and crusts. Sulphates include gypsum, halotrichite, melanterite type-phases, magnesiocopiapite, schwertmannite, and jarosite (Bobos et al, 2006). Many of these sulphates dissolve during rain events and subsequently re-form on drying periods. Also goethite and hematite occur in the substrate material. The dissolution of sulphide and the sulphate efflorescences led to production of low pH, metal rich-waters and the associated chemical and physical mobilization of heavy metals and metalloids to the local drainage system. According to Luis et al., (2009) surficial water samples of local streams, such as Água Azeda and Água Forte streams, affected by acid mine drainage (AMD) present low pH values (1.5 to 3.5) and high metal concentrations of As (6837 µg L⁻¹), Cd (455 µg L⁻¹), Cu (68795 µg L⁻¹), Fe (1262 mg L⁻¹), Mn (19,5 mg L⁻¹), Pb (136 µg L⁻¹), and Zn (264377 µg L⁻¹). This acid and soluble acid mine generation could be controlled by covering and sealing sulphidic mine waste with local no contaminated soil or by the removal of the waste material by burying the material in the former main shaft. Collection and treatment of AMD could be achieved by a physical and chemical plant or construction of a wetland environment plus anoxic lime drains. Revegetation of disturbed areas should be considered using imported topsoil and local plant species.

CONCLUSIONS

The results of soil analysis from the mining area of Aljustrel (South of Portugal), show elevated concentrations of metals. The median concentrations particularly for As, Cd, Cu, Pb and Zn are well above those of the regional baseline for world soils, the European Union and the Portugal and Andalusia. The same elements present concentrations that exceed the tentative guidelines set by Portugal and Andalusia Guide Values. Parent rock lithology and

mineralization seem to be the main factors influencing the abundance and distribution of trace elements. In some sites the concentrations of trace elements are significantly greater than the calculated threshold values. This may be ascribed to anthropogenic pollution, especially in Algaes and S. João do Deserto areas where it is difficult to distinguish human-induced pollution from natural mineralization.

The sequential extraction results showed that As, Cd, Cu, Pb and Zn metals were mainly found in the sulphide/clay mineral fraction of the soil while Co, Cr and Ni are mainly associated with the clay minerals and remaining silicates. Physical dispersion of sulphide minerals and also secondary metal-bearing minerals could be significant as revealed by the sequential extraction results. The chemical mobilization could also be pronounced for As, Cd, Cu, Pb and Zn because the bioavailable fractions could be significant.

Rehabilitation of disturbed areas should involve covering and sealing sulphidic mine wastes or removal of mining waste material, installation of a physical and chemical plant or construction of a wetland environment (plus anoxic lime drains), and import of topsoil and planting of local, metal-tolerant plant species.

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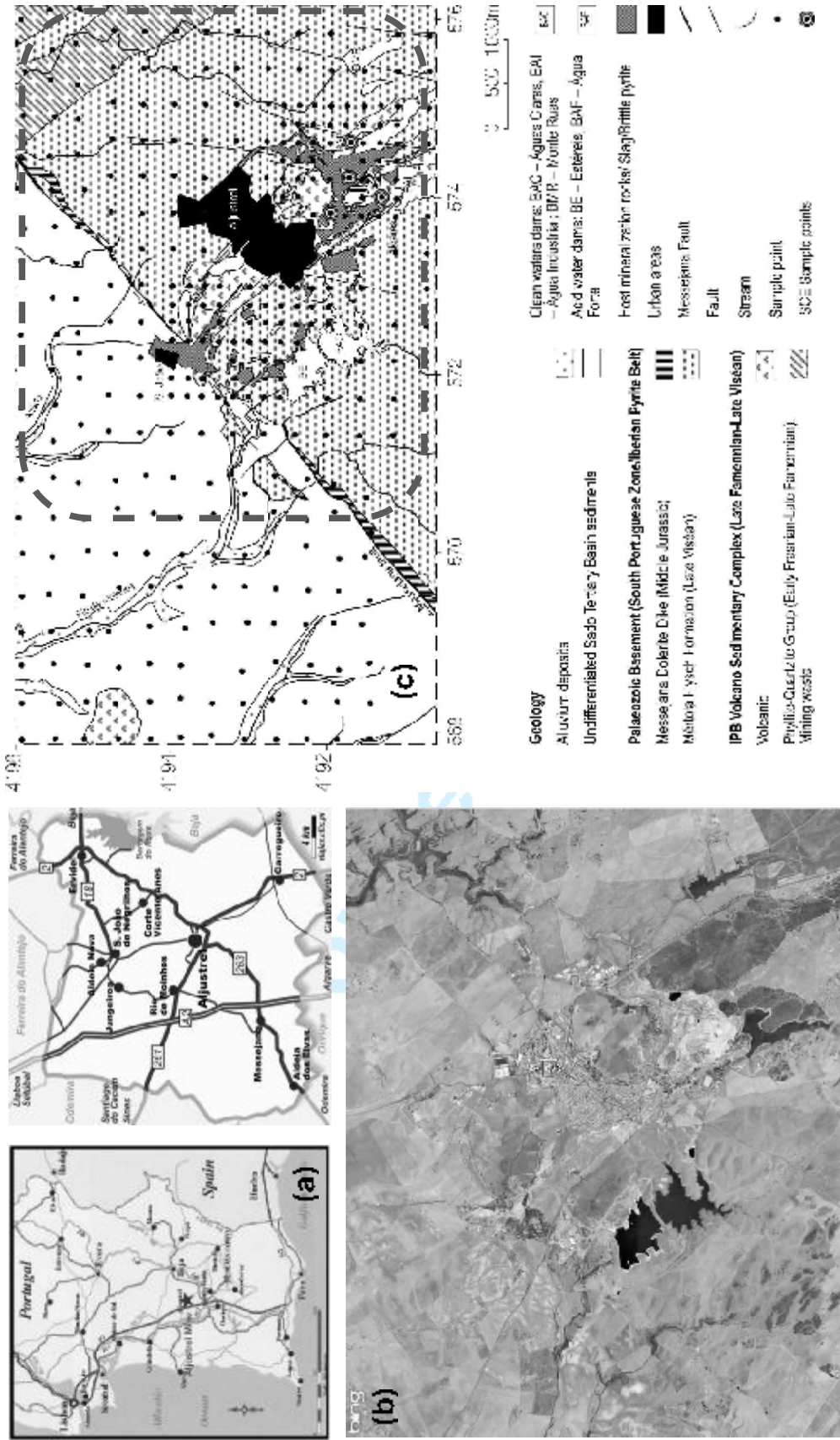


Figure 1. (a) Location of the Aljustrel study area and the detail of Aljustrel municipality (adapted from <http://google.brand.edgar-online.com/>; www.agenda.pt/frame.php?subcat=ALJUSTREL); (b) The orthophotomap gives a detailed view of the Aljustrel mining area (adapted from Map Viewer); (c) Geological setting and overlapping of the sampling grid (adapted from the Portuguese Geological Map 1:50000, Schermerhorn et al. 1987).

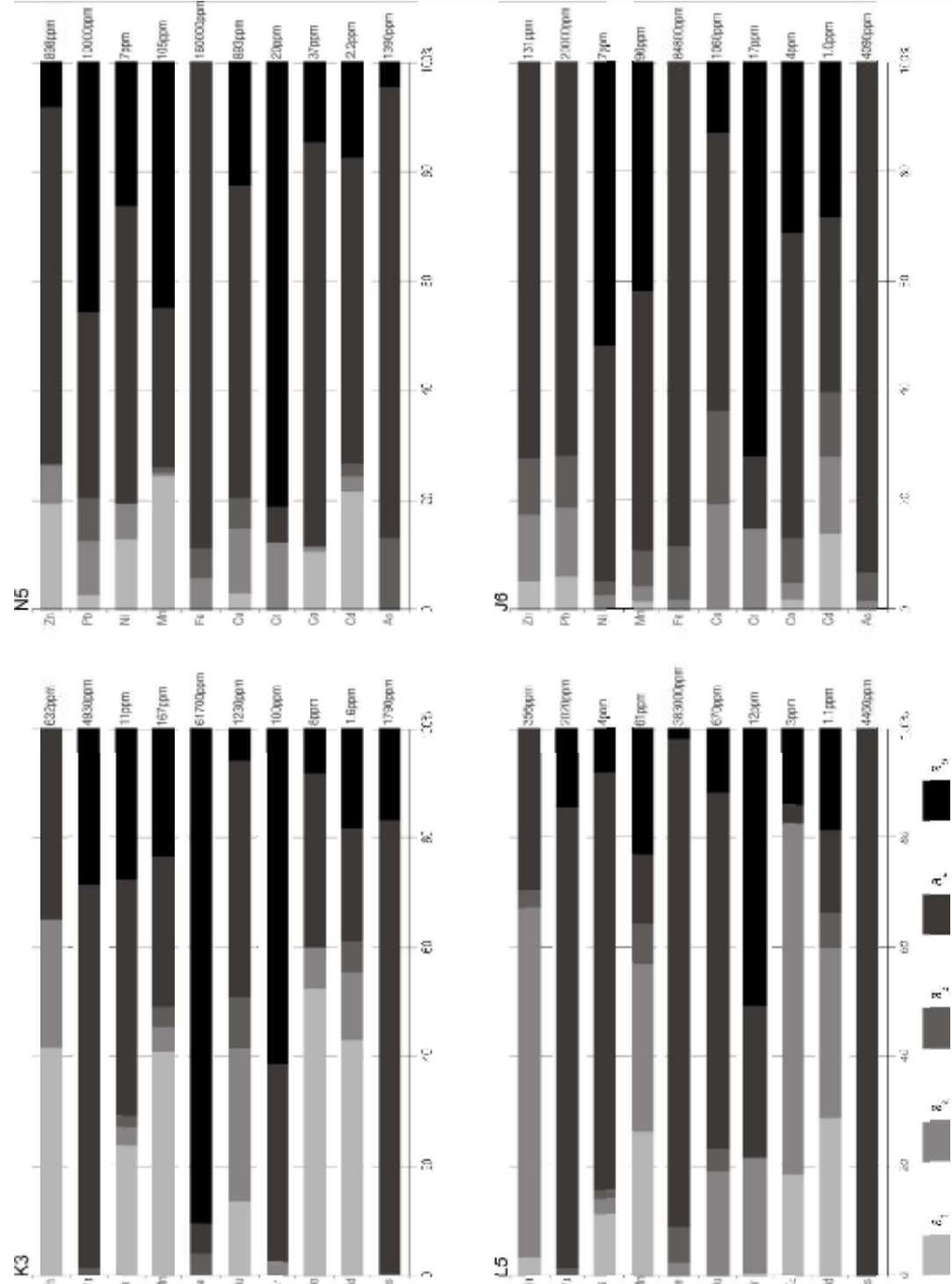


Figure 2. Metals, as a percentage of the total content, after fractionation through the SCE procedure: (a1) 1st Step - sodium acetate (NaOAc, pH 5); (a2) 2nd Step - cold hydroxylamine; (a3) 3rd Step - hot hydroxylamine; 4th Step - aqua regia; 5th Step - four acids digestion (or total attack).

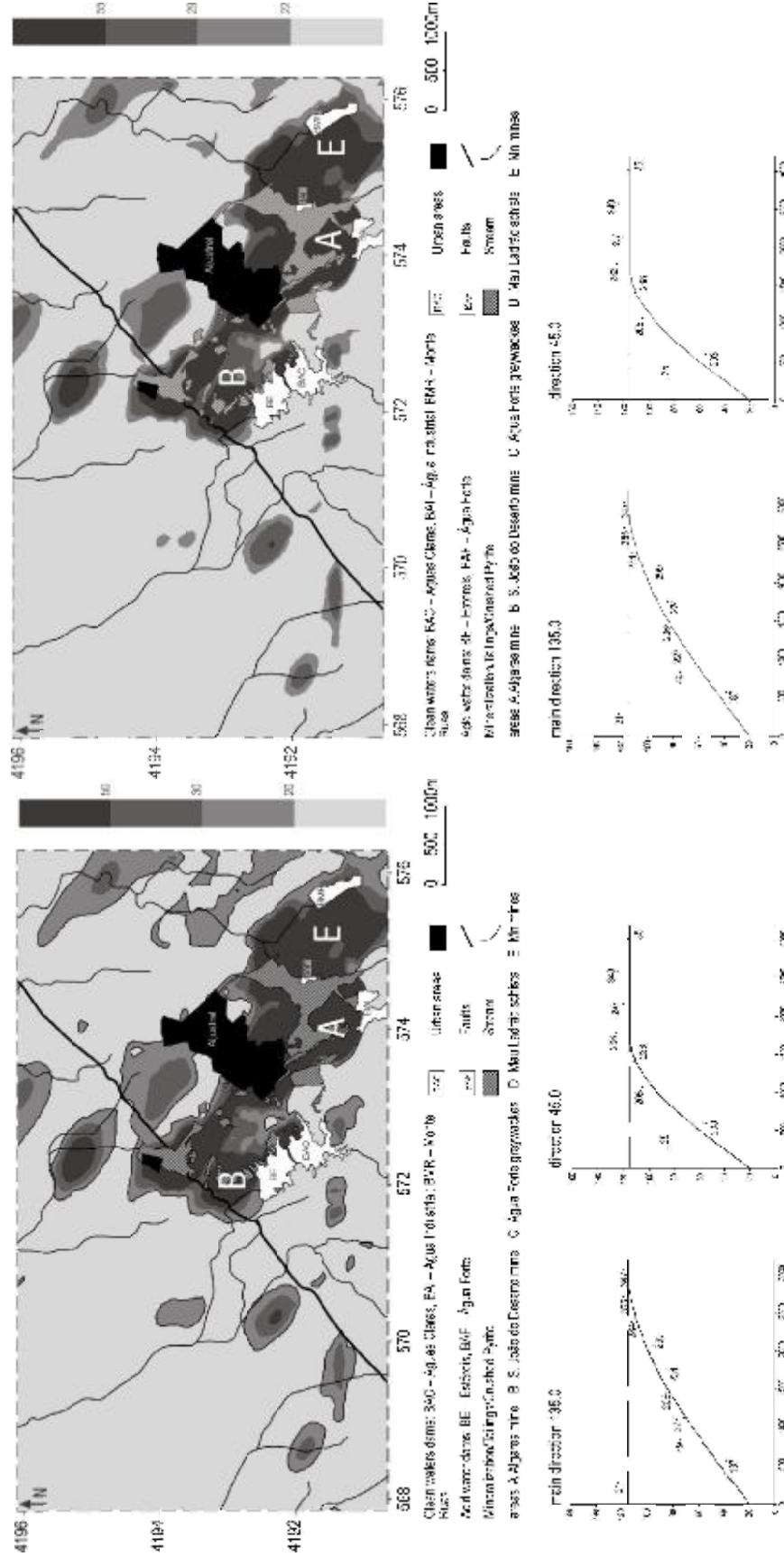


Figure 3. Mapping of As variables according the guide values and quality standards for assessing the quality of soils proposed by Aguilar et al (1999) for Ancaluzia and by Ferreira (2004) for Portugal [1st class: unpolluted; 2nd class: investigation is recommendable; 3rd class: investigation is obligatory; 4th soil reclamation is necessary].

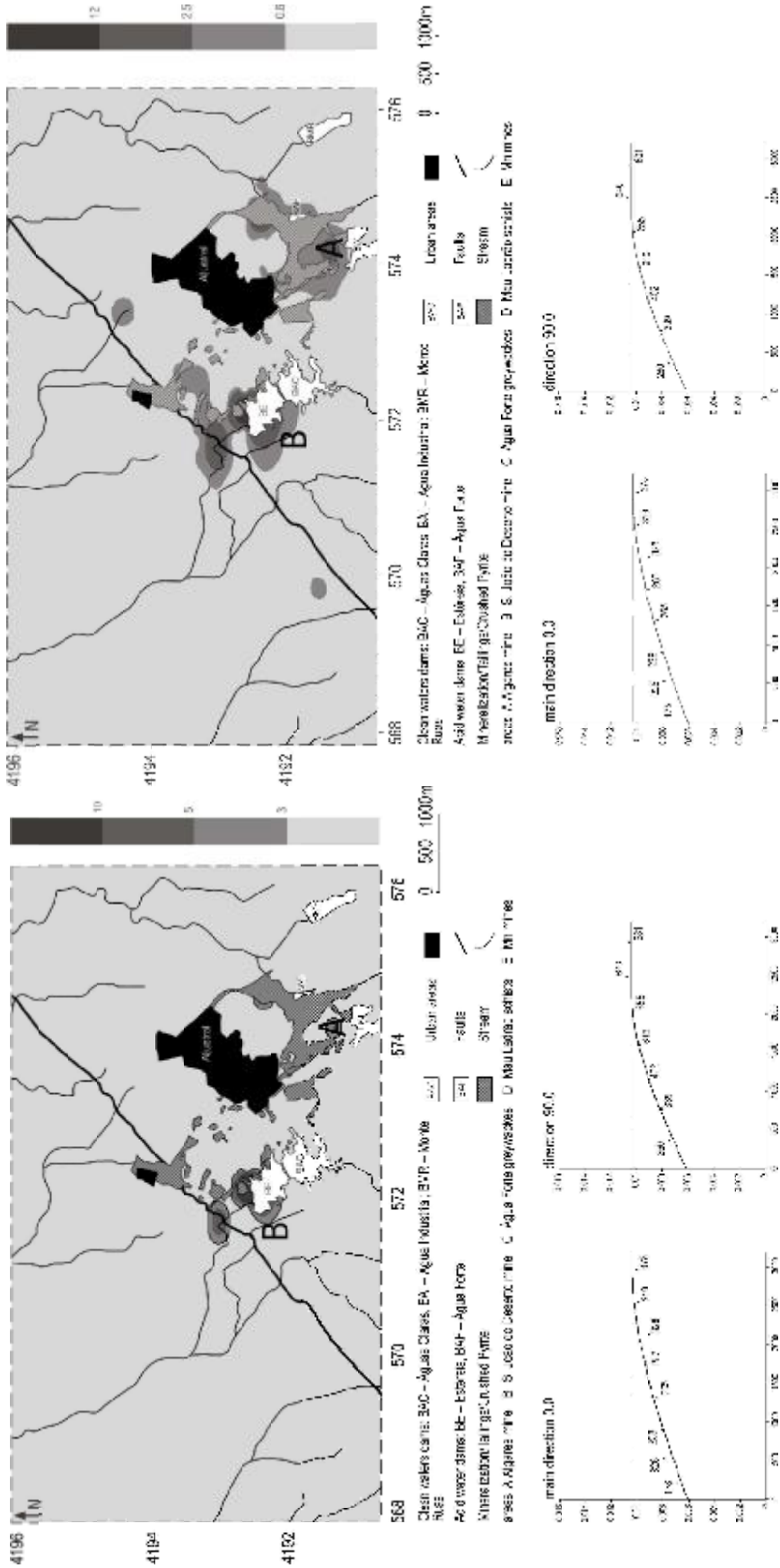


Figure 4. Mapping of Cd variables according to the guide values and quality standards for assessing the quality of soils proposed by Aguilar et al (1999) for Ancaluzia and by Ferreira (2004) for Portugal [1st class: unpolluted; 2nd class: investigation is recommendable; 3rd class: investigation is obligatory; 4th soil reclamation is necessary].

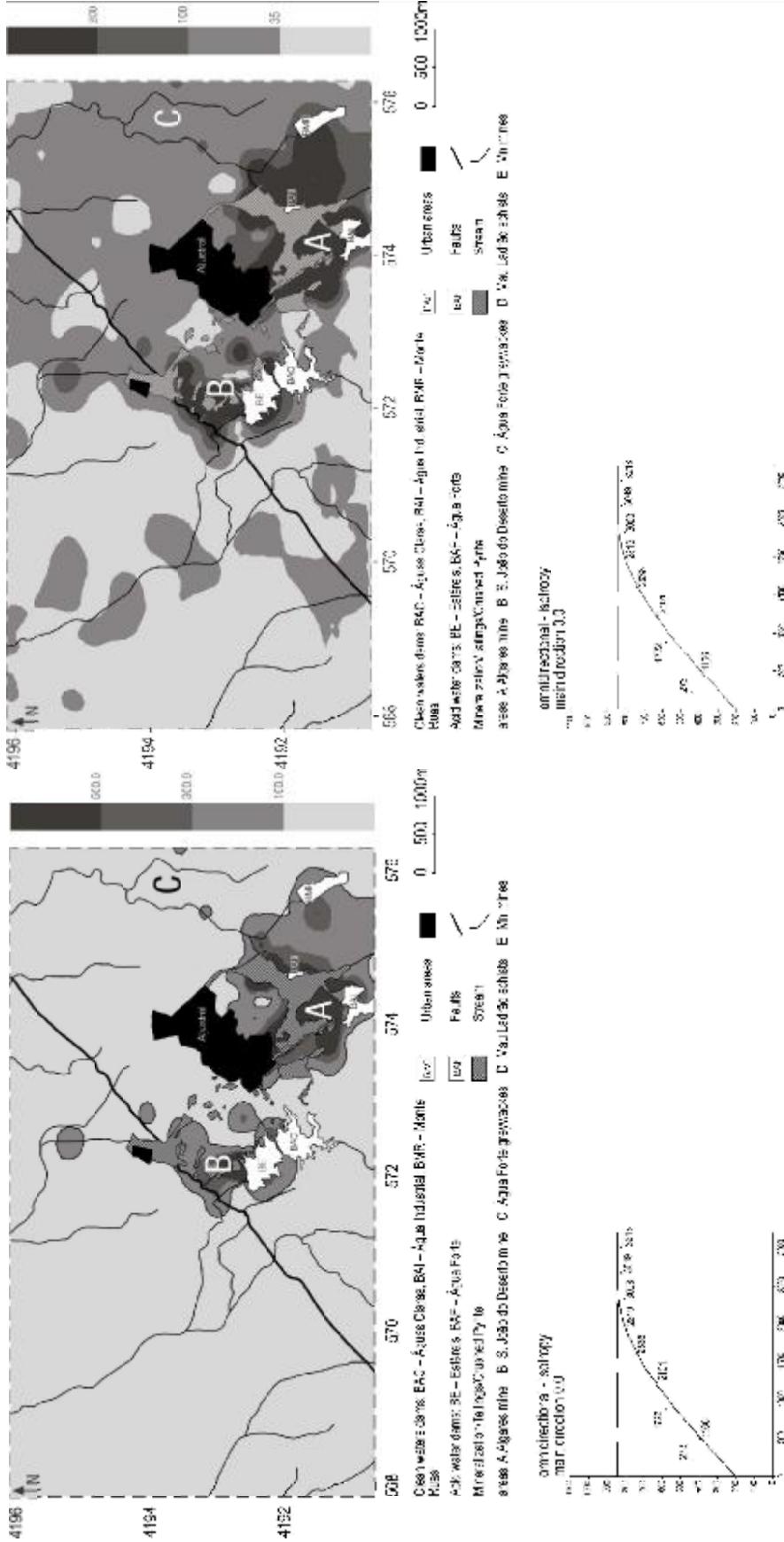


Figure 5. Mapping of Cu variables according to the guide values and quality standards for assessing the quality of soils proposed by Aguilar et al (1999) for Ancaluzia and by Ferreira (2004) for Portugal [1st class: unpolluted; 2nd class: investigation is recommendable; 3rd class: investigation is obligatory; 4th soil reclamation is necessary].

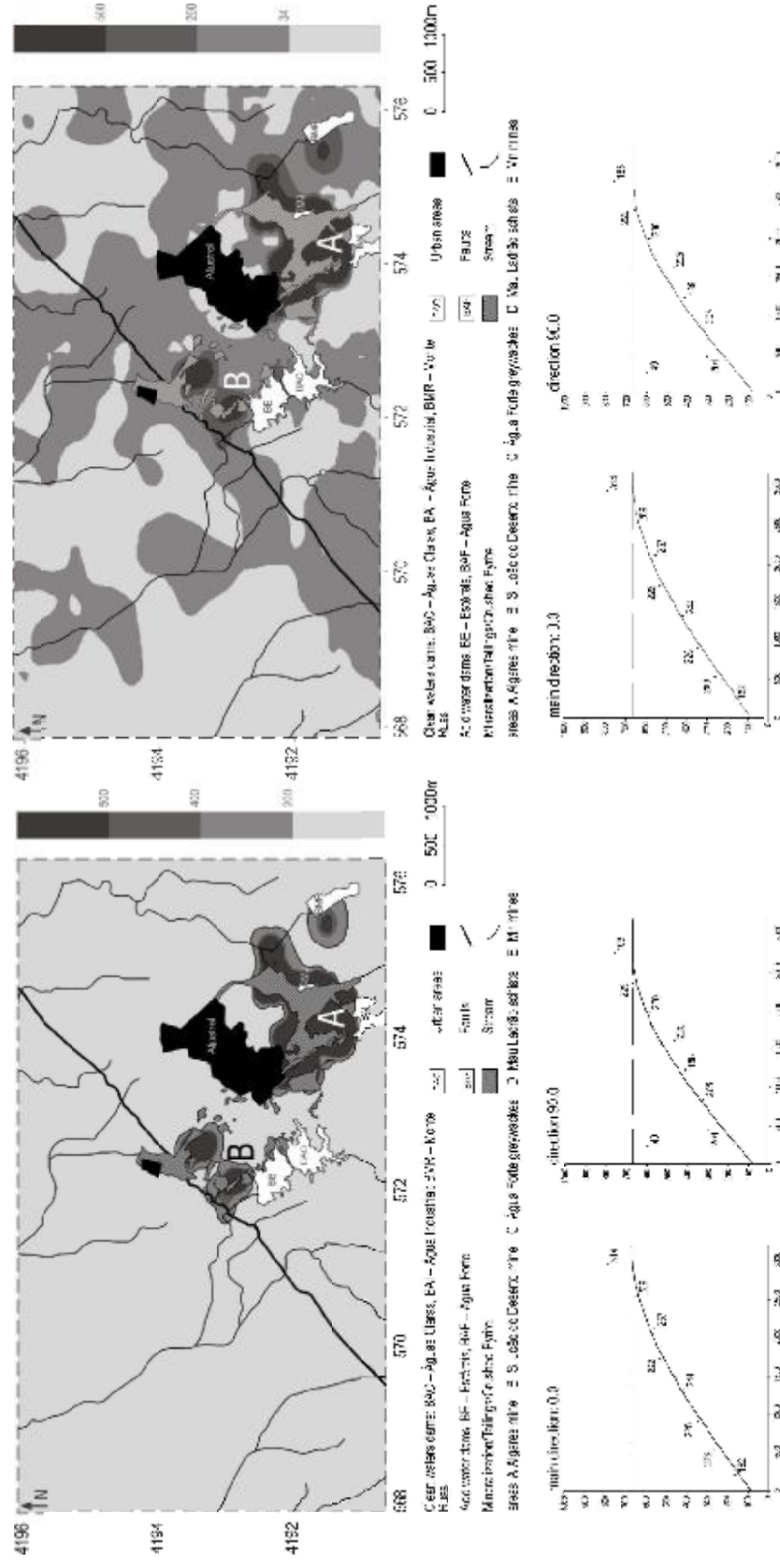


Figure 6. Mapping of Pb variables according the guide values and quality standards for assessing the quality of soils proposed by Aguilar et al (1999) for Ancaluzia and by Ferreira (2004) for Portugal [1st class: unpolluted; 2nd class: investigation is recommendable; 3rd class: investigation is obligatory; 4th soil reclamation is necessary].

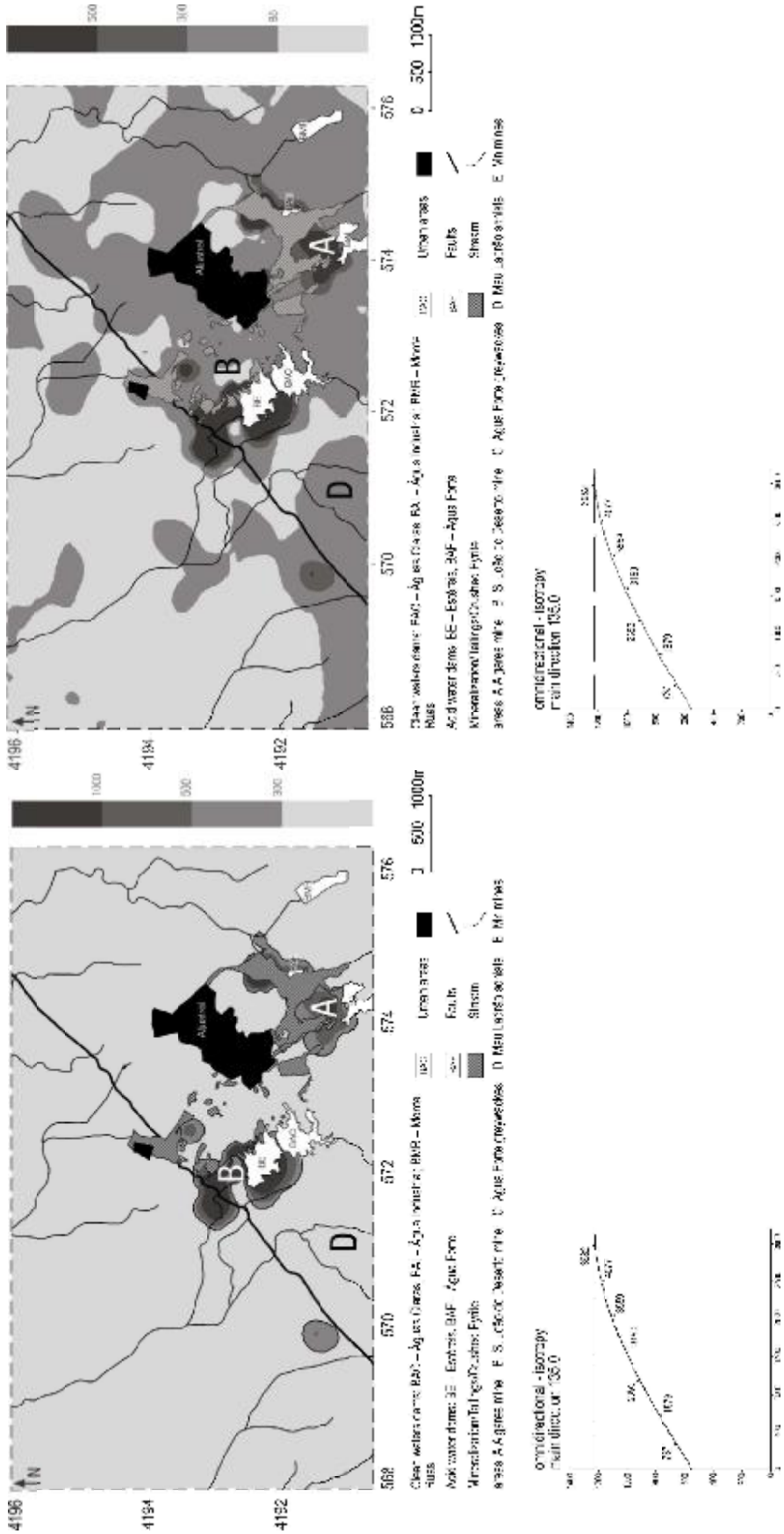


Table 1 – Descriptive basic statistics of potentially toxic elements in the Ajjustrel global database and according to the categorization to the parent rock lithology. Values are presented in mg kg⁻¹.

	Global data (n=356)					VSC (n=68)				USTB (n=151)				MD (N=6)				MFF (n=131)			
	Mean	Med	Min.	Max	Max	Mean	Med	Min.	Max	Mean	Med	Min	Max	Mean	Med	Min	Max	Mean	Med	Min	Max
As	99	13	6	3936	304	49	11	6	105	17	15	6	49	24	18	12	49	91	22	6	2573
Cd	0.6	0.2	0.1	61.5	9.6	0.3	0.1	0.1	0.9	0.2	0.2	0.1	0.9	2.2	0.4	0.1	11.7	0.9	0.3	0.1	61.6
Co	17	16	3	161	17	18	3	6	63	16	15	6	29	17	17	10	30	17	13	5	161
Cr	57	56	6	115	50	51	6	15	99	56	53	15	99	70	76	58	83	61	62	6	114
Cu	135	39	19	5414	264	110	22	10	186	32	29	10	186	89	35	21	357	169	53	11	5414
Ni	31	20	2	105	30	32	2	8	57	31	29	8	57	35	42	21	51	32	32	2	106
Pb	417	38	19	20000	1193	95	20	13	191	34	26	13	191	100	54	32	425	502	55	16	20000
Zn	239	88	22	23000	260	115	36	22	569	72	64	22	569	1237	158	43	6952	358	109	49	20000

VSC - Volcano-Sedimentary Complex; USTB - Undifferentiated Sado Tertiary Basin sediments; MD - Messejana Dolerites; MFF - Mértola Flysch Formation.

Table 2 Geochemical baselines of trace elements in Aljural area and some reference median values reported in worldwide soils, European Union, South Portuguese zone and Andalusia and guide values and quality standards for assessing soil contamination

Var	TS	GSM	Euro	SPZ	Andal.	PR	CSTC	Portuguese GV			Netherlands GV			Andalusia GV			
								BK	GV	IV	A	B	C	I	II	III	IV
As	18	5	7	25	10	25	20-50	11	22	55	20	30	50	<20	20-30	30-50	>50
Cd	0.2	1		n.a	n.a	n.a	n.a	<0.2	0.6	12		5	20	<3	3-5	5-10	>10
Co	16	10	8	19	12	19	25-50	8	19	50	20	50	300	<50	50-150	150-300	>300
Cr	66	80	60	95	70	95	n.a	21	43	300	100	250	800	<n.a	n.a	n.a	n.a
Cu	39	25	13	32	24	32	60-125	16	35	200	50	100	500	<100	100-300	300-500	>500
Ni	30	20	18	35	28	35	n.a	16	43	100	50	100	500	<n.a	n.a	n.a	n.a
Pb	38	17	23	37.9	24	38	100-400	21	34	500	50	150	600	<200	200-400	400-500	>500
Zn	88	70	52	75.8	56	76	70-400	55	85	500	200	500	3000	<300	300-500	500-1000	>1000

r.a. no available; TS median values for global data obtained in this study; GSM Global Soil Mean (Reimann and De Caritat, 1998); Eur. European Geochemical guidelines (Lovinson, 1980); SPZ South-Portuguese Zone geochemical baseline; Andal. Andalusia geochemical baseline; Galán et al., 2008; PR – Parent rock; CSTC Critical Soil Total Concentration (Kabata-Pendias and Pendias, 1992); Portuguese GV (Portuguese Guide Values according to Ferreira, 2004); MTS Metasediments; A. Ign. Igneous acid rocks; A. Bas. – Basic acid rocks; BK – Portuguese geochemical baseline; GV Guide value for Portuguese soils; IV – Intervention value (check the necessity of recovery/remediation); Netherlands GV (Netherlands Guide Values according to Alloway, 1995); A background value; B – Good for further investigation; C clean up definitely required; Andalusia GV (Andalusia Guide Values according to Aguiar et al., 1999; Galán et al., 2002); I maximum allowable values; investigation is recommended; intervention is needed.

Table 3 - Contamination factors (C_f) and modified degree of contamination (mC_f) using baseline values (median value for global data) and median values for heavy metals in each parent rock lithology

	As	Cd	Co	Cr	Cu	Ni	Pb	Zn	mC_f
Global data	5,50	3,00	1,06	1,02	3,46	1,03	10,97	2,65	3,59
VSC	6,20	2,00	0,94	0,98	2,40	0,94	11,93	2,26	3,46
USTR	1,13	1,00	1,07	1,05	1,10	1,07	1,21	1,13	1,10
MD	1,33	5,50	1,00	0,92	2,28	0,83	2,02	7,83	2,71
MFT	4,14	3,00	1,13	0,98	3,57	1,00	9,13	3,31	3,28
A gares area	20.2	5.9	1.1	0.6	8.6	0.5	54.2	7.4	12.3
S. João do Deserto area	4.7	30.2	2.0	1.1	6.3	1.3	8.0	29.8	10.4

Table 4 – Sample distribution between the different classes taking in consideration the Portuguese and Andalusian Guide Values [1st class: unpolluted; 2nd class: investigation is recommendable; 3rd class: investigation is obligatory; 4th soil reclamation is necessary].

	Portugal Guide Values				Andalusia Guide Values			
	Class 1	Class 2	Class 3	Class 4	Class 1	Class 2	Class 3	Class 4
As	40 (11.2%)	194(54.5%)	64 (18%)	58(16.2%)	213 (59,8%)	55 (15,4%)	28 (7,9%)	61 (17,1%)
Cd	207(58.1)	117(32.9%)	30(8.4%)	2(0.6%)	352 (98,9%)	0 (0,0%)	1 (0,3%)	3 (0,8%)
Cu	10(2.8%)	137(38.5%)	166(46.6%)	43(12.1%)	281(78,9%)	40 (11,2%)	16 (4,5%)	19 (5,3%)
Pb	40(11.2%)	246(69.1%)	69(19.4%)	1(0.3%)	317 (89,0%)	10 (2,8%)	5 (1,4%)	24 (6,7%)
Zn	63(17.7%)	110(30.9%)	166(46.6%)	17(4.8%)	330(92,7%)	9 (2,5%)	11(3,1%)	6 (1,7%)